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COMPLETE SPECIFICATION

Anti-tarnish Composition for Copper-containing Surfaces

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul 19, Minnesota, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described, in and by the following statement: —

This invention relates to a composition for treating tarnished copper-containing surfaces to remove tarnish and render the cleaned surface tarnish-resistant.

Copper-containing surfaces, including copper alloys such as bronze, brass, etc. are notoriously susceptible to discolouration due to tarnishing of the copper. A great variety of copper cleaners have been suggested for the removal of tarnish deposits, e.g. copper oxides and sulphides. However, the problem of inhibiting the tarnishing of the cleaned copper-containing surface through the use of diverse polymers, lacquers, oils and waxes has not provided prolonged tarnish resistance or has had other serious drawbacks, such as discolouration of the anti-tarnish protective coatings applied, difficulty in application or adverse effect on surface appearance.

It is a main object of the present invention to provide a composition which simultaneously cleans copper-containing surfaces and renders such surfaces tarnish-resistant for prolonged periods of time.

In accordance with this invention, a highly efficient composition for cleaning copper-containing surfaces and for rendering such surfaces tarnish resistant over an extended period of time comprises an aliphatic mercaptan of the formula $C_nH_{2n+1}SH$ wherein n is from 12 to 25, preferably from 16 to 21, and at least one non-abrasive copper-cleaning ingredient. If desired, other materials may be added to the composition, including suspending agents or surfactants, thickeners or viscosity improvers, abrasives, odourisers, solvent diluents and the like.

In cleaning copper-containing surfaces various non-abrasive ingredients have been used to remove the tarnish forming compounds by chemical action. Conventional copper cleaners frequently contain mild organic acids, such as citric or sulfamic acid, together with sodium chloride, various surfactants and abrasives. After dissolution of the tarnish deposits by the non-abrasive copper cleaning ingredients, which are usually acidic, and dislodging embedded tarnish by abrasive and/or surfactant action, if desired, the copper-containing surfaces are left in extremely reactive contact with the corroding environment. It is therefore preferable, for providing prolonged tarnish resistance, to accomplish the cleaning and the tarnish prevention simultaneously. Moreover, although abrasive-containing mercaptan formulations effectively clean and condition the tarnished surface, the concentration or "loading" of abrasive required to remove the tarnish deposits tends to remove the protective mercaptan film as it is formed. The presence of non-abrasive copper cleaning ingredients permits the elimination of, or a reduction in, the abrasive content of the formulation and provides significantly more effective tarnish resistance and a more efficient utilisation of the mercaptan compound.

It has now been found that aliphatic mercaptans of the above formula provide a thin, colourless, non-oily protective layer on clean copper-containing surfaces, bonding to the copper through the thiol grouping, and that such mercaptans may be incorporated into copper cleaning formulations to provide a protective layer on the copper substrate as the tarnish is effectively removed by the cleaning ingredients. The bond between the copper and the

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mercaptans is unusually strong, resisting washing with dilute alkaline or acid solutions, and with detergent solutions. Of equal importance is the colourless, transparent protective layer of these mercaptan molecules, which does not adversely effect the lustre of the copper-containing surface and which does not discolour or embrittle with aging. Moreover, although the film of mercaptan is virtually invisible to the naked eye, the presence of the protective layer may be detected by the hydrophobic or water repellent properties of the protected surface.

Both branched and straight chain aliphatic mercaptans may be employed, although the straight chain mercaptans are preferred. Mercaptans having less than twelve carbon atoms are not so desirable because of their somewhat greater volatility and greater difficulty in formulating with other desired cleaning ingredients. Mercaptans having more than twenty-five carbon atoms are not so desirable because they are higher melting solids and are more difficult to formulate. In general, these mercaptans have a mild odour which, if desired, may be masked with a suitable odouriser. They are non-toxic, particularly when considering the extremely minute quantities that are retained on the copper surface. Illustrative of the preferred mercaptans are n - hexadecane - 1 - thiol, n - dodecane - 1- thiol, n - octa - decane - 1 - thiol and n - heneicosane - 1 - thiol ($C_{21}H_{43}SH$).

Of the many non-abrasive copper cleaning ingredients which do not react with these mercaptans and which may be used in the anti-tarnish compositions of this invention the acidic cleaners are preferred because of their high efficiency. The various combinations of acidic ingredients suitable for cleaning copper-containing surfaces are well known. Generally, when using acidic cleaning ingredients in aqueous media, a pH of below 2.5 is preferred. The combination of a weak acid, e.g. citric acid, sulfamic acid, etc., and an alkali metal halide, e.g. sodium chloride, potassium chloride, etc., is an effective non-abrasive tarnish remover. Hydrochloric acid also is an effective non-abrasive copper cleaner. Since the anti-tarnish composition must be essentially non-oxidative, strong oxidising acids, such as nitric acid, should not be used. Acids having a pK between 1 and 5, which are water soluble, stable, non-oxidising acids which do not form water insoluble compounds with copper are preferred. Such suitable acids include the aliphatic, polybasic, hydroxy acids such as citric and tartaric which are non-toxic and non-irritating to the skin. Other suitable acids include acetic, formic, maleic and phosphoric.

The non-abrasive copper cleaners not only remove oxides from the tarnished copper surface but also permit the simultaneous formation of the continuous transparent film of the mercaptan compound. As mentioned earlier, when abrasives alone are employed in conjunction with the marcaptans, the abrading effect tends to remove or disrupt the continuity of the protective film. Although abrasives may desirably be used in addition to the non-abrasive copper cleaners, particularly when heavy sulphide tarnish deposits are encountered, they constitute less than 20 weight percent of the formulation and are preferably mild abrasives. Among the abrasive materials are finely divided silicas (including modified silicas), clays, diatomaceous earths, precipitated chalks. In addition, small quantities of surfactants, particularly the non-ionic variety, are usually employed. Viscosity improvers and thickeners may also be incorporated into the formulation, and such thickeners as colloidal alumina (i.e. AlOOH) and guar gum are particularly effective in acidic media. The selection of thickener usually is dependent on the pH of the composition, since various thickeners are more stable at a given pH value than others. Among the thickeners are the natural gums (e.g. locust bean gum, guar gum), carboxymethyl cellulose, sodium alginate, hectorite, etc.

The cleaning and tarnish preventative compositions of this invention may be formulated as a liquid, as a solid stick or as a paste. For certain uses it may be desirable to impregnate fabrics with these anti-tarnish compositions to provide a convenient applicator cloth. It is also possible to dispense these compositions from pressurised containers, e.g. aerosols, etc.

Although the mercaptan, or mixture of mercaptans, can be incorporated in varying amounts into the compositions of this invention, depending partly on the physical nature of the formulation, it has been found that mercaptan concentration within the 0.5 to 25, preferably 0.5 to 10, weight percent range is particularly effective in formulations containing a non-abrasive copper cleaner. Less than about 0.5 percent of mercaptan does not generally provide sufficient tarnish resistance.

In an aqueous liquid composition the most preferred formulations usually contain from 1 to 15 weight percent of mercaptan, 0.01% to 25% of a weak organic acid, 0.01% to 25% of an alkali metal halide (e.g. alkali metal chlorides, etc.) 0.05% to 1% of a surfactant, 0 to 20% of an abrasive, sufficient water to emulsify the mercaptan, and sufficient acid-stable thickeners to provide the desired viscosity.

The anti-tarnish composition may be applied to the copper-containing surface by spraying, dipping, roll coating, applicator cloth, etc. If an abrasive is included in the formulation, the copper surface is polished until the tarnish deposits are removed. When no abrasive is used, sufficient contact time is allowed to permit the copper cleaner to loosen and/or

remove the tarnish, preferably followed by buffing or wiping to bring out the lustre of the copper surface. The removal of all tarnish is essential to obtain the continuous protective film required for extended protection of the surface. In all instances, it is usually preferable to rinse the treated surface with water to remove any residual non-abrasive copper cleaner and abrasives. The following examples will illustrate the various preferred formulations, and their use and effectiveness in preventing the tarnishing of copper-containing surfaces for prolonged periods.

Example I

Test panels of copper and brass were degreased with trichloroethylene and polished with a commercial copper cleaner containing a non-abrasive copper cleaner, i.e. citric acid and sodium chloride, to remove all traces of tarnish. Immediately after cleaning (a water rinse is preferable), the dry copper-containing surfaces were sprayed with a one-percent solution of n-octadecane-1-thiol in petroleum ether and buffed with a soft cloth. The panels were then exposed to hydrogen sulphide at about 70% relative humidity along with cleaned uncoated control panels. A marked difference in tarnish rate was noticed, the deposits forming on the controls in less than 15 minutes and the coated panels remaining essentially tarnish free for several hours.

Example II

The procedure of Example 1 was repeated using n-heneicosane-1-thiol instead of n-octadecane-1-thiol. After exposure to the hydrogen sulphide atmosphere, the control panels (both copper and brass) tarnished in less than 15 minutes, whereas the treated panels were essentially tarnish free for several hours.

Example III

The following formulation was prepared, the percentages being by weight:

60% water
3% colloidal alumina (AlOOH)
10% n-octadecane-1-mercaptan
8% citric acid
8% sodium chloride
5% diatomaceous earth
5% 240 mesh silica
1% non-ionic surfactant

The colloidal alumina thickener was added to water and the temperature raised to 80° C. After mixing the mercaptan and the non-ionic surfactant and heating to 80° C., the mixture was added to the colloidal alumina solution with high speed mixing, forming a thick creamy emulsion. Once emulsification was complete, the citric acid and the abrasive were added with continued stirring until a homogeneous dispersion was obtained. Then upon adding the sodium chloride, immediate thickening to a smooth viscous paste occurred.

Copper panels were treated with the above formulation using a soft cloth, followed by water rinsing and air drying. Untreated copper panels which had been cleaned to remove tarnish were used as controls. After immersing both a treated and an untreated panel in a 1% aqueous solution of hydrogen sulphide, the untreated control was observed to tarnish after 5 seconds, whereas tarnishing of the treated panel occurred only after about 2 hours. A similar comparative test using a salt bath (5% aqueous sodium chloride) resulted in tarnishing of the untreated control in 30 minutes and no visible tarnishing of the treated panel after two days. Still another comparative test was made by placing both treated and untreated panels in a high temperature (212° F.) oxidative (air) environment, resulting in tarnishing of the untreated control in 10 minutes and tarnishing of the treated panel only after 6 hours. In each of the foregoing comparative tests the time reported is the time required for visible signs of tarnish to appear.

Example IV

Results similar to those in Example III are obtained with the following formulation:

76% water
2.5% hydrochloric acid
4% colloidal alumina
7½% diatomaceous earth
7½% 240 mesh silica
2.4% n-octadecane-1-mercaptan
0.1% non-ionic surfactant

Example V

Results similar to those in Example III are obtained with the following formulation:

2.5% colloidal alumina
2.4% n-octadecane-1-mercaptan
12% citric acid
12% sodium chloride
15% diatomaceous earth
1% non-ionic surfactant
55% water

Example VI

A composition for dip treatment of tarnished copper panels was prepared with the following ingredients:

6% n-octadecane-1-mercaptan
15% sodium chloride
15% citric acid
1% non-ionic surfactant
63% water

Tarnished copper panels were immersed in the above formulation, agitation being used to stabilise the dispersion. Tarnish deposits were removed within a few seconds. The panels were then rinsed with water. Excellent resistance to tarnishing over an extended period of time was noted.

As used herein the term "copper" includes "copper-containing" and covers, besides copper, such copper-containing alloys as brass

and bronze which contain significant quantities of copper.

WHAT WE CLAIM IS:—

1. A composition for treatment of a copper or copper-containing surface which comprises a mercaptan of the formula $C_nH_{2n+1}SH$ wherein n is from 12 to 25 and a non-abrasive copper-tarnish remover.

2. A composition according to Claim 1, wherein the copper-tarnish remover is a stable, water-soluble, non-oxidising acid having a pK between 1 and 5.

3. A composition according to Claim 2, in which the acid is citric or sulfamic acid.

4. A composition according to Claim 2 or Claim 3, which also contains an alkali metal halide.

5. A composition according to any preceding claim, wherein the mercaptan is:
n-hexadecane-1-thiol,
n-dodecane-1-thiol,
n-octadecane-1-thiol or
n-heneicosane-1-thiol.

6. A composition according to any preceding claim which also contains a surfactant.

7. A composition according to any preceding claim which also contains a mild abrasive in a proportion less than 20% by weight of the total composition.

8. A composition according to Claim 7, wherein the abrasive is finely divided silica or modified silica, clay, diatomaceous earth or precipitated chalk.

9. A composition according to any preceding claim, which also contains a thickening agent.

10. A composition according to Claim 1, which comprises 1 to 15% by weight of the mercaptan, 0.01 to 25% of an organic acid having a pK between 1 and 5, 0.01 to 25% of an alkali metal halide, 0.05 to 1% of a surfactant, 0 to 20% of an abrasive, sufficient water to emulsify the mercaptan and sufficient acid-stable thickener to provide a desired viscosity.

11. A composition according to claim 1 comprising, by weight:
60% water
3% colloidal alumina (AlOOH)
10% n-octadecane-1-mercaptan
8% citric acid
8% sodium chloride
5% diatomaceous earth
5% 240 mesh silica
1% non-ionic surfactant

12. A composition according to claim 1 comprising, by weight:
76% water
2.5% hydrochloric acid
4% colloidal alumina
7½% diatomaceous earth
7½% 240 mesh silica
2.4% n-octadecane-1-mercaptan
0.1% non-ionic surfactant

13. A composition according to claim 1 comprising, by weight:
2.5% colloidal alumina
2.4% n-octadecane-1-mercaptan
12% citric acid
12% sodium chloride
15% diatomaceous earth
1% non-ionic surfactant
55% water

14. A composition according to claim 1 comprising, by weight:
6% n-octadecane-1-mercaptan
15% sodium chloride
15% citric acid
1% non-ionic surfactant
63% water

15. A method of cleaning a tarnished copper or copper-containing surface which includes the step of applying to the surface, from which the tarnish has been removed, a mercaptan of the formula $C_nH_{2n+1}SH$ in which n is from 12 to 25 to retard retarnishing of the surface.

16. Compositions for cleaning copper and copper-containing surfaces substantially as herein described with reference to any of Examples 3 to 6.

17. A method according to Claim 15, substantially as herein described with reference to any of Examples 1 to 6.

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